



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 1 487 940 B1**

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
14.06.2006 Bulletin 2006/24

(21) Application number: **03724936.4**

(22) Date of filing: **27.03.2003**

(51) Int Cl.:
C10G 11/18 (2006.01)

(86) International application number:
PCT/EP2003/003244

(87) International publication number:
WO 2003/080766 (02.10.2003 Gazette 2003/40)

(54) **PROCESS FOR COMBUSTING COKE DURING REGENERATION OF A FCC CATALYST.**

VERFAHREN ZUR VERBRENNUNG VON KOKS BEI DER REGENERIERUNG EINES FCC-KATALYSATORS.

PROCEDE DE COMBUSTION DU COKE

(84) Designated Contracting States:
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IT LI LU MC NL PT RO SE SI SK TR**

(30) Priority: **27.03.2002 US 368066 P**

(43) Date of publication of application:
22.12.2004 Bulletin 2004/52

(73) Proprietor: **SHELL INTERNATIONALE RESEARCH
MAATSCHAPPIJ B.V.
2596 HR Den Haag (NL)**

(72) Inventors:
• **DIRKKS, Jacobus, Mathias, Hendrikus
NL-1031 CM Amsterdam (NL)**
• **HIGGINS, Richard, Joseph
Norco, LA 70079 (US)**
• **SAMSON, Rene
NL-1031 CM Amsterdam (NL)**

(56) References cited:
US-A- 4 325 817

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 1 487 940 B1

Description

[0001] The present invention pertains to a process for combusting coke of a coke-containing FCC catalyst in a regeneration unit of a FCC unit and to a corresponding apparatus for performing said process.

[0002] Fluidized catalytic cracking (FCC) processes operate by circulating catalyst particles continuously from a reactor in which a hydrocarbon feed is cracked to lower boiling products, during which cracking carbonaceous material is deposited on the catalyst, via a regenerator in which the carbonaceous material is combusted to restore the catalyst activity, to heat up the catalyst (necessary to supply heat for the endothermic cracking reactions on the reactor side) and returning catalyst particles to the reactor. Such a process and reactors for performing these processes are known in the art. Reference is made to Robert A. Meyers, Handbook of Petroleum Refining Processes, McGraw-Hill (1996), particularly Part 3, pp. 3.3-3.112.

[0003] The present invention relates to the regeneration step in the FCC-process. In this step the carbonaceous material ("coke") that has been formed on the surface and in the pores of the catalyst during the reaction step is (partly or completely) removed from the catalyst by combustion with an oxygen-containing gas.

[0004] In this combustion process, inevitably the catalyst is irreversibly damaged. This damage is accelerated by high temperatures, high steam partial pressure and by certain contaminants (principally vanadium- and nickel-containing compounds), which stem from the hydrocarbon feedstock and which are deposited on the catalyst during the cracking reactions. In order to maintain the catalytic activity at a certain level, it is customary to replace a certain amount of the catalyst inventory from the unit by fresh catalyst on a regular basis. The term "regular" in this context refers to the frequency with which this replacement is carried out. Depending on the degree of automation of the FCC unit, the time interval between catalyst replacements may vary from a few minutes to a few days.

[0005] Refiners have taken several measures to reduce the irreversible damage to the catalyst as much as possible. This damage is called "hydrothermal deactivation" because of the prominent role of temperature and steam. One commonly employed stratagem is to limit the amount of contaminants on the catalyst. Many refiners maintain a closely watched upper limit on e.g. the amount of vanadium and nickel on the catalyst and adjust their catalyst replacement rate (the so-called "make-up rate") so that this upper limit is not exceeded.

[0006] It is more difficult to regulate temperature and steam partial pressure in the regenerator. The regenerator temperature is not a practical instrument in this respect, since this is dictated by the heat balance of the unit (the heat requirements on the reactor side). Steam partial pressure likewise is not simple to control. A large amount of the steam in the regenerator is a coproduct of

the combustion reactions and hence is dictated by the amount of coke burnt, which again is dictated by the heat balance of the unit.

[0007] Some refiners have found a way around this problem, which is conceptually sound but very costly. Their solution is to split the combustion process over two different vessels. It is well known (see the above mentioned handbook of Meyer, p. 3.91) that hydrogen burns faster than carbon. As a result, the majority of the steam is generated in the first stage of the combustion process. By staging the combustion, one achieves a situation in which the majority of the steam is generated at a relatively low combustion temperature in the first stage, while the final temperature-increase in the second stage takes place at a relatively low steam partial pressure. Since it is the combination of a high temperature and a high steam partial pressure, which is particularly harmful for the catalyst, this method of combustion limits the hydrothermal deactivation of the catalyst. The downside of this method is that it implies a very substantial increase in capital cost of the unit. In addition, one extra vessel also implies more transport lines for the catalyst, which are always vulnerable pieces of equipment that frequently give rise to operational problems.

[0008] There is therefore a need for a much simpler and much less costly stratagem, which achieves the same goal, namely diminishing the rate of catalyst deactivation.

[0009] The present invention has to its object to provide improved combustion of coke at low hydrothermal deactivation, which is suitable in any regenerator, including in a one-stage regenerator. The invention relates to a method and an apparatus wherein oxygen-containing gas, preferably air, is cooled before introduction into the regeneration unit.

[0010] The invention resides in a process for combusting coke of a coke-containing FCC catalyst in a regeneration unit of a FCC unit comprising the introduction of oxygen-containing gas through a gas transport unit into the regeneration unit and combusting the coke by means of the oxygen-containing gas, characterized in that the oxygen-containing gas is cooled in a cooling unit (8) to a temperature below the dew point of water present in the gas thereby giving condensation of water, wherein the condensed water is separated from the gas before it is brought in contact with the coke-containing FCC catalyst.

[0011] The cooling unit allows the gas transport unit to transport more gas in terms of weight to the regeneration unit increasing the capacity of the regeneration process. Adding a cooling step to an existing FCC regenerator process is thus a method to increase the capacity of such an unit.

[0012] Cooling furthermore lowers the dew point of water present in the gas, thereby giving condensation of water. This condensed water is suitably separated from the gas before the gas is used in the regenerator process. The oxygen-containing gas therefore contains less water

than non-cooled gas. It was found that this was very beneficial for the average lifetime of the catalyst, since less catalyst was irreversibly destructed by hydrothermal deactivation of the (zeolite) catalyst at the high temperatures (typically around 680 °C) that are used in the regeneration process. Reduction of moisture in the oxygen-containing gas, for instance, from 2.8 wt% to 0.8 wt% or less is easily obtainable with the present process.

[0013] From a practical standpoint it is preferred that the oxygen-containing gas is cooled before or during its stay in the gas transport unit. More preferably the oxygen-containing gas is cooled before its stay in the gas transport unit.

[0014] The oxygen-containing gas may be any gas that contains oxygen, and most preferably such oxygen-containing gas is air.

[0015] In another aspect the invention pertains to a method for decreasing the thermal deactivation of a catalyst in an FCC regeneration process, characterized in that the regeneration process is performed by applying the above-mentioned process.

[0016] In yet another aspect the invention pertains to an apparatus for performing the above process comprising a reactor unit with inlet and outlet means, a regenerator unit with inlet means that are connected to the reactor unit and outlet means that are connected to the inlet means of the reactor unit, characterized in that the apparatus further comprises a gas transport unit located in or at inlet means of the regenerator unit, and a cooling unit in the transport unit or upstream the transport unit at its suction side.

[0017] The invention is further described in the following Figures, without construing these Figures as to limit the invention in any way.

[0018] Fig. 1 is a block scheme of an apparatus of the invention;

[0019] In Fig. 1 a reactor unit (not shown) forms a cycle with regenerator unit 2. The fluid catalyst continuously is transferred from reactor unit 1 to regenerator unit 2, and from regenerator unit 2 back to reactor unit 1 through inlet and outlet means 3, 4, 5. Through inlet means 6 air (or another oxygen-containing gas) is introduced into the regenerator unit 2 for use as oxygen source in the coke combustion. Regenerator unit 2 and reactor 1 are kept on the required temperature and pressure with means that are commonly used in these processes. Air is continuously introduced by using gas transport unit 7, which upstream is provided with a cooling unit 8. Transport unit 7 is preferably an air blower such as known to the skilled person, for instance from Perry's Chemical Engineers' Handbook; 6th Edition (1984). See pages 6-24, which deal with rotary blowers. This is the type of machine that preferably is used to compress FCC air. The air that is sucked is cooled by using a cooling unit 8. The cooling unit 8 is preferably located upstream at the suction side of the blower 7, but in other types of gas transport units 7 cooling may also be performed within the gas-transport unit 7. Between cooling unit 8 and gas transport unit 7 a

separation vessel 10 is present to separate water via 11 from the cooled air. Among the cooling units 8 that may be used are conventional industrial chillers, for instance those as have been described in Perry's Chemical Engineers' Handbook; 6th Edition (1984); pages 11-28. These chillers may be referred to as refrigeration machines. The energy for these machines can be either provided by a steam turbine or electrically. It will depend on local refinery conditions which form of energy supply is the preferred route. Usually these machines are cooled by cooling fluids such as freon or ammonium. Cooling machines that use water as coolant may also be used.

[0020] The regenerator 2 in Figure is also provided with a dense fluidized bed 12, cyclone separators 13 and gas outlet 14.

[0021] The process of the invention typically provides temperature differentials from 35 to 10 °C. The effect is the greatest in summer and in countries with a hot (humid) climate. Preferably the temperature of the air before being cooled is higher than 25 °C, more preferably higher than 30 °C. The advantages of the invention are especially found when the content of water in air before cooling is between 50 and 100% and preferably between 75 and 100% of total saturation (humidity). The following is an illustrative example of the benefits of this invention. In a unit with a feed intake of 16,000 t/d (tons/day) (typical coke burn rate = 870 t/d; typical catalyst make-up rate = 7 t/d); the reduction in catalyst make-up rate reduction during the summer months would be 0.8 t/d; and during the winter months: 0.2 t/d. The yearly average reduction in catalyst make-up rate is 0.4 t/d; corresponding to roughly 300,000 \$/year savings of catalyst consumption.

Claims

1. A process for combusting coke of a coke-containing FCC catalyst in a regeneration unit of a FCC unit comprising the introduction of oxygen-containing gas through a gas transport unit (7) into the regeneration unit (2) and combusting the coke by means of an oxygen-containing gas, **characterized in that** the oxygen-containing gas is cooled in a cooling unit (8) to a temperature below the dew point of water present in the gas thereby giving condensation of water, wherein the condensed water is separated from the gas before it is brought in contact with the coke-containing FCC catalyst.
2. The process according to claim 1, wherein the oxygen-containing gas is cooled before or during its stay in the gas transport unit.
3. The process according to claim 2 wherein the oxygen-containing gas is cooled before its stay in the gas transport unit.
4. The process according to any one of claims 1-3

wherein the oxygen-containing gas is air.

5. The process according to claim 4, wherein the air has a temperature higher than 25°C, preferably higher than 30°C.
6. The process according to any one of claims 4-5, wherein the air has a water content before cooling of between 50 and 100% of total saturation, preferably between 75 and 100% of total saturation.
7. The process according to any one of claims 4-6, wherein the air is cooled with a temperature differential from 35 to 10°C.
8. The process according to any one of claims 1-7 wherein the gas transport unit (7) is an air blower.
9. The process according to any one of claims 1-8 wherein cooling is performed in an industrial chiller (8).
10. A method for decreasing the thermal deactivation of a catalyst in an FCC regeneration process, **characterized in that** the regeneration process is performed by applying the process according to any one of claims 1-9.
11. A regenerator apparatus for performing the process according to claims 1-9 comprising inlet and outlet means (3, 4, 5, 14), and an inlet (6), wherein the apparatus further comprises a gas transport unit (7) located in or at inlet means (6) of the regenerator unit (2), a cooling unit (8) in the transport unit or upstream the transport unit at its suction side and between cooling unit (8) and transport unit (7) a separation vessel (10) is present to separate water via (11) from the cooled air.

Patentansprüche

1. Verfahren zur Verbrennung von Koks eines kokshaltigen FCC-Katalysators in einer Regeneriereinheit einer FCC-Einheit, bei welchem ein sauerstoffhaltiges Gas durch eine Gastransporteinheit (7) in die Regeneriereinheit (2) eingebracht und der Koks mittels eines sauerstoffhaltigen Gases verbrannt wird, **dadurch gekennzeichnet, daß** das sauerstoffhaltige Gas in einer Kühleinheit (8) auf eine Temperatur unterhalb des Taupunktes des im Gas vorhandenen Wassers abgekühlt wird, wodurch es zu einer Kondensierung von Wasser kommt, wobei das kondensierte Wasser von dem Gas getrennt wird, bevor es mit dem kokshaltigen FCC-Katalysator in Kontakt gebracht wird.
2. Verfahren nach Anspruch 1, bei welchem das sauerstoffhaltige Gas vor oder während seines Aufenthaltes in der Gastransporteinheit gekühlt wird.

erstoffhaltige Gas vor oder während seines Aufenthaltes in der Gastransporteinheit gekühlt wird.

3. Verfahren nach Anspruch 2, bei welchem das sauerstoffhaltige Gas vor seinem Aufenthalt in der Gastransporteinheit gekühlt wird.
4. Verfahren nach einem der Ansprüche 1-3, bei welchem das sauerstoffhaltige Gas Luft ist.
5. Verfahren nach Anspruch 4, bei welchem die Luft eine Temperatur höher als 25°C, vorzugsweise höher als 30°C, hat.
6. Verfahren nach einem der Ansprüche 4-5, bei welchem die Luft vor der Kühlung einen Wassergehalt zwischen 50 und 100 % der Gesamtsättigung, vorzugsweise zwischen 75 und 100 % der Gesamtsättigung, hat.
7. Verfahren nach einem der Ansprüche 4-6, bei welchem die Luft mit einer Temperaturdifferenz von 35 bis 10°C gekühlt wird.
8. Verfahren nach einem der Ansprüche 1-7, bei welchem die Gastransporteinheit (7) ein Luftgebläse ist.
9. Verfahren nach einem der Ansprüche 1-8, bei welchem die Kühlung in einem Industriekühler (8) durchgeführt wird.
10. Verfahren zum Absenken der Wärmedeaktivierung eines Katalysators in einem FCC-Regenerieverfahren, **dadurch gekennzeichnet, daß** das Regenerieverfahren durchgeführt wird, indem das Verfahren nach einem der Ansprüche 1-9 angewendet wird.
11. Regeneriervorrichtung zur Durchführung des Verfahrens nach einem der Ansprüche 1-9, mit Einlaß- und Auslaßmitteln (3, 4, 5, 14) und einem Einlaß (6), wobei die Vorrichtung ferner eine Gastransporteinheit (7) aufweist, die in oder bei den Einlaßmitteln (6) der Regeneriereinheit (2) angeordnet ist, eine Kühleinheit (8) in der Transporteinheit, oder stromaufwärts der Transporteinheit an deren Saugseite, und wobei zwischen der Kühleinheit (8) und der Transporteinheit (7) ein Abscheidegefäß (10) vorhanden ist, um das Wasser über (11) von der gekühlten Luft zu trennen.

Revendications

1. Procédé de combustion du coke d'un catalyseur FCC contenant du coke dans une unité de régénération d'une unité FCC consistant à introduire du gaz contenant de l'oxygène par l'intermédiaire d'une unité de transport de gaz (7) dans l'unité de régénération.

tion (2) et à brûler le coke au moyen d'un gaz contenant de l'oxygène, **caractérisé en ce que** le gaz contenant de l'oxygène est refroidi dans une unité de refroidissement (8) à une température inférieure au point de rosée de l'eau présente dans le gaz, suscitant ainsi la condensation de l'eau, dans lequel l'eau condensée est séparée du gaz avant qu'elle ne soit mise en contact avec le catalyseur FCC contenant du coke.

5

10

2. Procédé selon la revendication 1, dans lequel le gaz contenant de l'oxygène est refroidi avant ou pendant son séjour dans l'unité de transport de gaz.

3. Procédé selon la revendication 2, dans lequel le gaz contenant de l'oxygène est refroidi avant son séjour dans l'unité de transport de gaz.

15

4. Procédé selon une quelconque des revendications 1 - 3, dans lequel le gaz contenant de l'oxygène est de l'air.

20

5. Procédé selon la revendication 4, dans lequel l'air a une température supérieure à 25 °C, de préférence supérieure à 30 °C.

25

6. Procédé selon une quelconque des revendications 4 - 5, dans lequel l'air a une teneur en eau avant refroidissement comprise entre 50 et 100 % de saturation totale, de préférence comprise entre 75 et 100 % de saturation totale.

30

7. Procédé selon une quelconque des revendications 4 - 6, dans lequel l'air est refroidi avec un différentiel de température de 35 à 10 °C.

35

8. Procédé selon une quelconque des revendications 1 - 7, dans lequel l'unité de transport de gaz (7) est une soufflante d'air.

40

9. Procédé selon une quelconque des revendications 1 - 8, dans lequel le refroidissement est effectué dans un refroidisseur industriel (8).

10. Procédé pour diminuer la désactivation thermique d'un catalyseur dans un procédé de régénération FCC, **caractérisé en ce que** le procédé de régénération est mis en oeuvre en appliquant le procédé selon une quelconque des revendications 1 - 9.

45

50

11. Dispositif de régénération pour mettre en oeuvre le procédé selon les revendications 1 - 9 comprenant des moyens d'entrée et de sortie (3, 4, 5, 14) et une entrée (6), dans lequel le dispositif comprend en outre une unité de transport de gaz (7) située dans ou au niveau du moyen d'entrée (6) de l'unité de régénérateur (2), une unité de refroidissement (8) dans l'unité de transport ou en amont de l'unité de

55

transport sur son côté aspiration et une cuve de séparation (10) est présente entre l'unité de refroidissement (8) et l'unité de transport (7) pour séparer l'eau (11) de l'air refroidi par l'intermédiaire du (11).

Fig.1.

